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EFFECTS OF INTERMOLECULAR BONDING ON THE DRAWING BEHAVIOR OF NYLON 66

A THESIS

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EFFECTS OF INTERMOLECULAR BONDING ON THE

DRAWING BEHAVIOR OF NYLON 66

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SUMMARY

Water has a very pronounced effect on the drawing behavior of nylon; however, aqueous solutions of organic acids, mineral acids, urea, and methyl alcohol have much smaller effects on the drawing behavior compared with the effect of water alone. The concentrations of these chemicals were not sufficiently high to cause appreciable changes in the drawing behavior and, thus, provided little insight into the mechanism of the drawing process.

Phenol, on the other hand, is strongly sorbed by the fiber from its aqueous solutions and caused very significant changes in the drawing behavior of the fiber. The mechanical data and phenol absorption data obtained in this work add support for the structural model for nylon as described by Zaukelies (6). His model considers nylon to be highly crystalline having a high (but not unreasonably high) concentration of lattice vacancies and dislocations.

The introduction of water in nylon breaks sufficient hydrogen bonds in the polymer to decrease the yield load approximately fifty per cent. The sorption of phenol from aqueous solutions does not cause an appreciable change in the yield load up to a phenol concentration of approximately 1.5 moles per kilogram of fiber. This finding is interpreted as due to a simple replacement of water molecules in the polymer by phenol with no attendant effect on the drawing behavior. If the concentration of phenol is increased beyond 1.5 moles per kilogram of fiber, there is a rapid decrease in the yield load. The interpretation for this result is that

a second type of sorption is operative, one which involves the diffusion of phenol into the more highly ordered (crystalline) parts of the polymer, resulting in an appreciable change in the drawing behavior.

CHAPTER I

INTRODUCTION

Statement of Problem

The drawing of undrawn nylon 66 produces a stress-strain curve with a characteristic yield point. This is followed by a flat portion of the curve where the fiber extends with little or no increase in the load above that at yield point. In this flat portion of the curve the fiber does not usually draw uniformily, but draws through the formation of "necks". The yield stress and maximum drawability are a function of the previous thermal history of the polymer (1) and the moisture content of the fiber (2).

In this work a study has been made to determine how the drawing behavior of nylon is altered by the presence of chemicals which can affect intermolecular bonding in the polymer, particularly those chemicals which can break hydrogen bonds. These chemicals include water, organic acids, mineral acids, urea, alcohols, and phenol. The effects of dyeing on the drawability of nylon have also been studied.

The purpose of this work was to investigate the mechanical behavior of these modified fibers. It is believed that variations in the mechanical behavior due to the presence of various chemicals that have been absorbed should provide some insight into the mechanism of the drawing process.

Review of Literature

Nylon 66 was discovered by Wallace C. Carothers. It is the condensation polymer of adipic acid, $HOOC(CH_2)_4COOH$, and hexamethylene diamine, $H_2N(CH_2)_6NH_2$. Each of these substances has six carbon atoms and for this reason the resulting product, poly(hexamethyleneadipamide), is called nylon 66.

To prepare a textile yarn from the polymer, it is melted and extruded. The yarn is then drawn or extended about three times its original length. Fankuchen and Mark determined from x-ray studies of nylon before and after drawing that there is a great increase in the molecular order of the nylon as it is drawn (3). In further x-ray studies, Bergmann, Fankuchen, and Mark found that drawing produces increased molecular orientation at the expense of crystalline perfection (4). Bunn and Alcock state that the crystallinity is due to the ease with which the polyamide chains fit together in a regular manner locking the chains together with the formation of hydrogen bonds between regularly spaced amide groups (5).

The most generally accepted model for describing the structure of semi-crystalline polymers has been that they consist of small crystallites embedded in a matrix of amorphous polymer (6). Modifications of this "crystalline-amorphous" model are variously referred to as "the fringed micelle" and "fringed fibril" models.

Zaukelies (6) has proposed a new model for the structure of crystalline polymers such as nylon 66 and 610. His model is that the polymer consists essentially of completely crystalline material containing numerous vacancies, dislocations, and grain boundaries. Although this

model has been described specifically for nylon 66 and nylon 610, he states that, presumably, the model should be suitable for other highly crystalline polymers.

Much work has been done on the cold-drawing of amorphous and semi-crystalline polymers in an attempt to develop a theory to explain the phenomenon, but none of the theories give suitable explanations for all of the aspects of cold-drawing. The effects of various chemicals on the drawing behavior of nylon has been studied by Quynn (7). In his work the effects of n-heptane, air, carbon tetrachloride, diethyl ether, chloroform, acetone, ethanol, methanol, ethylene glycol, and water were studied; however, in his work the fibers were not immersed in the various media during the drawing. Quynn states that his results indicated that the character of the drawing process does not change on passing from air to inert, non-polar liquids. In general, there was an increasing tendency toward cold drawing and a reduction in the yield load as the polarity of the liquid increased. This was in agreement with the work of Forward (8). Hookway states that the yield load was directly related to the molecular mobility. He also said that changes in the moisture content, temperature, and density of an undrawn sample will change the yield load and drawing load (2).

Through x-ray studies of nylon 66, Sakuma and Rebenfeld found that drawing increases the molecular order mainly along the fiber axis during the early stages of drawing and then mainly in the lateral direction after a certain level of orientation had been achieved. They also stated that as the fiber swelled due to an increase in the moisture content or due to the presence of other chemicals, the fiber became less dense and

weaker (9). The work done by Bergmann, Fankuchen, and Mark demonstrated the same effects (4).

Carlene, Fern, and Vickerstaff found that, as the dye concentration of acid dyes in the fiber was increased, the drawing or yield stress remained almost the same while the breaking stress decreases substantially. As the breaking stress decreases, the extent of drawing decreases until the breaking stress becomes the yield load. They state that the acid dyes bring about the development of an electrical charge on the amide groups due to the absorption of hydrogen ions. The dye acts like a cross link preventing the orientation of the polymer chains when drawing is attempted.

CHAPTER II

INSTRUMENTATION AND CHEMICALS

Undrawn "15 denier" monofilament nylon 66 made by the Monsanto Company was used in this work. All of the samples came from a single end from the same bobbin. The measured denier of the nylon filament was 66.

The Instron Model TTC tensile tester was used to determine the stress-strain properties of the nylon filament. In order to determine the drawing behavior in liquids, a special lower clamp was made for the Instron from type 316 stainless steel as shown in Figure 1. A one-eighth diameter stainless steel rod with a hook on each end was used for the upper jaw. The A-load cell of the Instron was used with possible full scale loads of 10, 20 and 50 grams. A 2-liter resin pot was set on a ring stand so that the resin pot could be moved up and around the sample and the upper jaw. The ring stand was attached to the lower beam of the Instron with a 10 inch C-clamp.

Dyes used were C. I. Acid Red 1, C. I. Acid Blue 45, C. I. Direct Blue 28, and C. I. Direct Blue 1. Table 1 shows the chemical structures of these dyes.

The following chemicals were used:

Eastman Cement 910
Glacial Acetic Acid, 99.7%
Urea, 99.9%
Butanol, 99.9%
Sodium Carbonate, 99.9%
Hydrochloric Acid, 37.7%
Formic Acid, 90.8%
Sodium Nitrite, 99.4%
Sodium Hydroxide Pellets, 98%

Weighings were made with either a Mettler type H6T or Mettler P160 balance.

The constant temperature bath consisted of an Arthur L. La Pine and Company heater-stirrer unit attached to a circular glass bath filled with Carbo-Wax 400. Agitation was provided by a Burrel Wrist-Action Shaker.

For determining the amount of dye and phenol sorbed by nylon, a Beckman DB-G grating spectrophotometer with a Beckman 10-inch laboratory recorder and hydrogen lamp power supply was used. A 1.000 cm fused silica cell was used with the dyes and a 4.000 cm fused silica cell was used with phenol.

A Corning Research pH meter was used for measuring the pH of the aqueous solutions.

For determining the lateral swelling of nylon fibers a Carl Zeiss Microscope with an American Optical Filar Micrometer Eyepiece was used. The eyepiece was calibrated with an American Optical Company 2 mm micrometer slide.

CHAPTER III

PROCEDURES

Preparation and Drawing of Nylon 66 Samples

Preparation and Conditioning of the Nylon 66

The undrawn nylon was all taken from the same bobbin and the same end on that bobbin. Suction provided by an aspirator was used to remove the nylon from the bobbin. To insure uniformity in the structure of the fiber and to remove impurities in the nylon, it was boiled for twenty-five hours in distilled water. The nylon used in dyeing was boiled again in a 2.0 g/l aqueous solution of sodium carbonate for thirty minutes to remove impurities not removed by the boiling water. The nylon was then rinsed many times in fresh distilled water to make certain all of the sodium carbonate was removed. Before using the nylon, it was dried and stored in a room at a temperature of 70°F. and a relative humidity of 65%.

Mounting the Nylon Samples

In the initial stages of this work five-mil nylon 66 film was used; however, a problem of slippage of the film in the jaws of the Instron was encountered and could not be resolved. Therefore, a nylon 66 monofilament was then used since its smaller size required a lower load for drawing. A new method for holding the sample had to be developed since the samples were to be tested in liquid media and the usual clamping methods for the Instron could not be used.

Fiber-mounting tabs were cut from a sheet of phosphor-bronze, one thirty-second of an inch thick. They were cut one-half inch in length and one-fourth inch in width. A hole five-thirty seconds of an inch in diameter was drilled at one end of the tab, centered with respect to the width. This hole made it possible to hang the tab from the one-eight inch stainless steel rod, which constituted the upper jaw of the Instron. The tabs were then sanded to remove any jagged edges. To remove grease and dirt from the surface of the tabs, they were boiled for one hour in a methanol-chloroform mixture (50/50 by volume). The tabs were then rinsed in methanol and left to dry in the air. The weight of the tabs was approximately 0.3 gram.

A jig for mounting fibers was made out of a sheet of Plexiglass. A piece of the Plexiglass approximately ten inches in length and three inches in width was cut out and set on legs so the mounting surface was elevated about two inches. One inch squares were cut out of the Plexiglass and glued onto the mounting surface centered with respect to the width of the mounting surface. In the length direction, Plexiglass squares were spaced approximately one-eighth inch apart.

The tabs with the hole in them were placed on one side of the mounting surface and the solid tabs were placed on the other side directly across from the tab with the hole and separated by the one inch plexiglass squares on the mounting surface. The tabs were arranged so that when the nylon filament was laid across the width of the mounting surface between two of the one inch squares it would bisect the two tabs on opposite sides of the one inch squares. One end of the nylon was then taped to the mounting surface and the other end was taped to a small

paper clip weighing 0.3 grams. The end of the nylon with the paper clip was left hanging freely over the edge of the mounting surface so the nylon would be held in position to facilitate the cementing of the fiber to the tabs using Eastman Cement 910. After the cement had dried the nylon was cut at the outer edge of the tabs and what remained was the sample, two tabs with a one inch nylon filament between them.

Drawing the Sample

All of the stress-strain properties were determined in the same manner. In all drawing experiments made with the fiber immersed in various liquids, the temperature of the liquids was maintained at 70° F. When the drawing was made in air, the conditions were 70° F, 65% relative humidity. A two liter resin pot was part of the Instron setup, and was held on a ringstand. The ringstand was secured to the Instron with a C-clamp. A sample was removed from the solution and placed in the jaws of the Instron and then the resin pot was raised around the sample covering the sample with solution. When the sample was tested in the air, the resin pot was raised around the sample to prevent air currents in the room from affecting the drawing. The total time required for this operation did not exceed one minute, and to compensate for this the sample was allowed to set in the solution for an additional five minutes before continuing with the measurement.

A one gram pre-stress was applied to the sample and then the cross-head of the Instron Tester was activated. The Instron Tester was set up with a cross-head speed of 0.5 in/min, a chart speed of 1.0 in/min, a 1.0 inch guage length (the distance between the tabs) and a full scale load of 10, 20, or 50 grams. Thus, the rate of extension was fifty per

cent per minute. Results of the load applied to the sample were plotted in grams versus the elapsed time of the test corresponding to the amount of strain the sample had undergone.

Effects of Various Solutions on the Drawing Behavior of Nylon 66

The fiber samples were placed in two liter bottles containing the appropriate solutions and were left in the closed containers for twenty-four hours (see Table 2). No more than twelve samples were used in the two liters of solution to insure that the change in the concentration of the solution due to the sorption of the chemicals by the samples would be negligible. At the end of the conditioning period the samples were tested in the solutions.

Effects of Phenol on Nylon 66

Drawing Behavior of Nylon 66 in Phenol Solutions

Nylon samples mounted on tabs were placed in two liter bottles containing aqueous solutions of phenol, 2.5 g/l, 5.0 g/l, 7.5 g/l, 20 g/l, 30 g/l, 40 g/l and 50 g/l. The samples remained in these solutions forty-eight hours. The samples were then drawn in the phenol solutions.

Lateral and Longitudinal Swelling of Nylon 66 in Phenol Solutions

For measuring the lateral and longitudinal swelling of nylon 66 in the phenol solutions, a filament of nylon approximately eighteen inches long was mounted between two small phosphor bronze tabs weighing 0.09 - 0.11 gram. The sample was attached to a glass hook and then placed in a burette. The distance between the tabs or the length of the filament was measured dry inside burette by counting the number of etched marks between the tabs. Then a solution of phenol was carefully added to the

burette and the length of the filament was measured at intervals of five minutes for sixty minutes and then at thirty minute intervals for two hours. From a knowledge of the length of the filament dry and in phenol the per cent swelling in the longitudinal direction was calculated.

To investigate the longitudinal swelling further it was decided that swelling the nylon in water prior to being placed in aqueous phenol solutions would provide more insight into the swelling. The nylon was placed in distilled water and allowed to come to equilibrium, and the length of the nylon filament was measured as before. The water was then replaced by an aqueous solution of phenol and the additional swelling determined. Carrying this idea further the longitudinal swelling was measured in distilled water and then in increasing concentrations of aqueous phenol.

To measure the lateral swelling, a short length of the nylon filament was placed on a slide with some of the phenol solution. Its diameter was measured microscopically using a calibrated micrometer eyepiece. Diameters of the dry sample and phenol treated samples were compared and the per cent lateral swelling was calculated.

Amount of Phenol Absorbed by the Nylon 66

To relate the phenol absorption to drawing and swelling, knowledge of the actual amounts of phenol absorbed is required. In order to obtain this information a stock solution of phenol (50 g/l) in distilled water was prepared by dissolving 25.005 grams of "Crystal Phenol" in 500 ml. of distilled water. By diluting the stock solutions with distilled water, solutions containing 40 g/l, 30 g/l, 20 g/l, 10 g/l, 7.5 g/l, 5.0 g/l, and 2.5 g/l were prepared. A solution of NaOH(.01N) was used for diluting the phenol solutions and as the reference in making spectrophotometric

measurements. A calibration curve was prepared for the phenol by recording the absorbance for four solutions of phenol differing in concentration (0.002 g/l, 0.0025 g/l, 0.0050 g/l, and 0.0075 g/l). The solutions were scanned between wavelengths of 340 mμ and 240 mμ. The maximum absorption was found at a wave length of 290 mμ. The absorbance at the wavelength of 290 mμ was plotted against concentration to establish the calibration curve as shown in Figure 2.

The amount of phenol absorbed by the nylon was found by determining the change in the concentration of phenol due to its sorption by the fiber. To do this, weighing bottles with ground glass tops were filled with 50 ml of each of eight aqueous phenol solutions (50 g/l, 40 g/l, 30 g/l, 20 g/l, 10 g/l, 7.5 g/l, 5.0 g/l, or 2.5 g/l). A known weight of the nylon 66 filament (approximately 1.000 g) was then placed in each of the bottles. The nylon was left in the bottle for fifty-eight hours after which time the nylon was removed. The solution was diluted with 0.01N NaOH and its absorbance measured.

From the calibration curve for the phenol solutions it was determined that the specific absorbance, that is, the absorbance for 1 g/l at 290 mμ and a cell thickness of 1.000 cm., was 27.1. Calculations of the amount of phenol absorbed were then made as follows:

A_i = initial absorbance

A_f = final absorbance

f = dilution factor

w = sample weight in grams

$$\text{Initial Concentration of Phenol} = A = \frac{A_i\ (f)\ g}{(27.1)\ (4)\ 1} = A$$

$$\text{Initial Amount of Phenol} = B = \frac{A_i\ (f)\ (50)\ g}{(27.1)\ (4)\ (1000)} = B$$

$$\text{Final Concentration of Phenol} = C = \frac{A_f\ (f)\ g}{(27.1)\ (4)\ 1} = C$$

$$\text{Final Amount of Phenol} = D = \frac{A_f\ (f)\ (50)\ g}{(27.1)\ (4)\ (1000)} = D$$

$$\text{Amount of Phenol Absorbed} = E \quad B - D = \frac{A_i\ (f)\ (50)\ g}{(27.1)\ (4)\ (1000)} -$$

$$\frac{A_f\ (f)\ (50)\ g}{(27.1)\ (4)\ (1000)} = E$$

$$\text{Amount of Phenol Absorbed by Nylon} = F = \frac{E(1000)\ g}{w \quad kg} = F$$

$$\text{Partition Coefficient} = K = \frac{F}{C} = \quad K = \frac{50\ (A_i - A_f)}{w\ \ (A_f)}$$

Effects of Dyeing on the Drawing Behavior of Nylon 66

C. I. Acid Red 1

A stock solution of Kiton Red 2G (C. I. Acid Red 1) was prepared having a concentration of 0.3 grams of dye per liter of distilled water. Nine dyebaths were prepared each having a total volume of 50 ml. The compositions of these dye baths are given in Table 3. The dyeings were made in 100 ml volumetric flasks with ground glass tops. The flasks were shaken continuously for two hours at 90° C. The nylon was then removed from the dyebath and rinsed quickly in distilled water and left to dry for twenty-four hours in air. After drying, the samples were mounted on tabs and tested in air on the Instron.

C. I. Acid Blue 45

A stock solution of Alizarine Sapphire BN (C. I. Acid Blue 45) was made having a concentration of 0.3 grams of dye per liter of distilled water. A calibration curve was then prepared for the dye by recording the absorption spectra of the dye at four concentrations by diluting the stock solutions with 0.1N NaOH. The absorbance at a wavelength of 600 mμ, which corresponds to maximum absorption was then plotted against the concentration to establish the calibration curve as shown in Figure 3.

Six dye baths were prepared with 20 ml of dye stock solution, 5 ml of distilled water, and 25 ml of an acid in each bath. Duplicate dye baths were prepared, one being used for dyeing and the other one retained as a reference. The dyeings were made in 100 ml volumetric flasks for two hours at 90° C. After dyeing, the nylon was removed and dried for twenty-four hours before being mounted for drawing. The compositions of the dye baths are shown in Table 4.

The amount of dye sorbed was found by measuring the difference between the absorbance of the final dye bath and the reference solution. For these measurements the dye solutions were diluted with 0.1N NaOH and 0.1N NaOH was used as a spectrophotometric reference.

The per cent dye sorbed by the fiber was determined using the formula:

$$\% \text{ dye in fiber} = \frac{\frac{50}{1000}\left(D_i - \frac{A_f \cdot f}{a}\right)}{w}$$

Where D_i = Concentration of dye in the dyebath initially (g/l)

A_f = Absorbance of the final dyebath

f = Dilution factor

a = Specific absorbance of a 1 g/l concentration of dye measured with a 1.000 cm path length at 600 mμ

w = Sample weight (g)

C. I. Direct Red 28

A stock solution of DuPont Congo Red (C. I. Direct Red 28) was prepared having a concentration of 0.1 gram of dye per liter of distilled water. A 2% o.w.f. (based on weight of fiber) and a 10% o.w.f. solution of dye and nylon were prepared and the pH of the solutions was adjusted to seven using 0.1N NaOH. The dye solution and nylon were boiled for twenty-four hours. The nylon was then removed and dried for twenty-four hours in air. The nylon filaments were then mounted on tabs and drawn on the Instron Tester in air (see Table 5).

C. I. Direct Blue 1

A stock solution of DuPont "Pontamine" Sky Blue FF (C. I. Direct Blue 1) was prepared having a concentration of 0.1 gram of dye per liter of distilled water. Two dyebaths were prepared, 2% and 10% dye based on the weight of fiber to be dyed. The dye solutions were adjusted to a pH of 3.7 by adding acetic acid and then nylon was added. The solutions were boiled for twenty-four hours. The nylon was then removed and air dried for twenty-four hours, mounted on tabs, and drawn on the Instron in air (see Table 6).

Part of the nylon samples dyed with C. I. Direct Red 28 and C. I. Direct Blue 1 were placed in flasks containing 0.02N HCL and boiled for one hour. The pH of the solutions was 1.6. The samples were then air dried for twenty-four hours, mounted on tabs, and drawn on the Instron in air.

CHAPTER IV

RESULTS AND DISCUSSION OF RESULTS

General Observations of Drawing Behavior of Nylon

When an undrawn filament of nylon was drawn using the Instron Tester, the formation of a neck was observed at a low extension. On extending the filament further, the neck moved toward the ends of the specimen and when the extension exceeded about 200 per cent, the neck disappeared. Multiple necks observed by other investigators were not found in this work. Following the characteristic level portion of the stress-strain curve where cold drawing is said to be taking place, the load necessary for drawing increased and slippage of the filament from the tabs became a problem. The samples could not be drawn to break because of this problem of fiber slippage. Hookway maintains that the breaking load and extensibility are not suitable parameters for undrawn fibers because jaw slippage at high tensions is difficult to avoid (2). He employed the yield and drawing loads for describing the drawing behavior of nylon. These characteristics of the stress-strain curves have been adopted for this work.

Vincent states that the ratio of the yield load to the drawing load is a useful measure of the cold drawing tendency of a fiber, with increasing values of the ratio above unity indicating a greater inclination toward cold drawing (10). This ratio was included in all the tables in this work that deal with the yield and drawing loads.

Effect of Water, Aqueous Solutions of Acids and Methanol on the Drawing Behavior of Nylon

It is well known that water has a great effect on the mechanical behavior of polymers with which it can interact by secondary bonding. For example, Meredith found that at zero per cent humidity the specific stress was 60 gwt/tex, at 65 per cent humidity the specific stress was 50 gwt/tex, and at 100 per cent humidity the specific stress was 45 gwt/tex (11).

The apparent melting point of nylon 66 in water or the temperature at which a nylon filament completely loses its shape is approximately 180° C, whereas, its melting point in the dry state is 250° - 260° C. It was decided that an investigation would be made of the drawing behavior of nylon in water and aqueous solutions of chemicals known to interact strongly with nylon, for example, organic and mineral acids, methanol, and phenol. Formic acid, hydrochloric acid, and some phenols used in this work are known solvents for nylon.

Since the affinity of phenols for nylon is much greater than the affinity of organic and mineral acids, and its effect on the drawing behavior is more pronounced, a discussion of the effect of aqueous phenol solutions is given separately in the section which follows.

Table 2 includes the experimental results obtained when nylon is drawn in various aqueous and methanolic solutions. In all cases the yield and drawing loads are much lower than those obtained when the drawing is made in air. Water alone decreases the yield load from 30.3 g to 17.2 g and the ratio of the yield load to the drawing load increases from 1.07 to 1.14. The stress-strain curves are shown in Figure 4. With respect to drawing in aqueous solutions of hydrochloric, acetic, and formic

acids, the results are very similar to those obtained with water alone. If more concentrated solutions had been employed, it is certain that very significant changes in drawing would have occurred since two of these acids, formic and hydrochloric, are solvents for the polymer. The highest concentrations of these acids used were as follows:

hydrochloric acid	0.1N
acetic acid	100 g/l
formic acid	20 g/l

When methanol was used, the yield and drawing loads were significantly lower than those for water alone, 15.3 g and 13.3 g compared with 17.2 g and 15.1 g respectively. For a 50/50 mixture of methanol and water the yield and drawing loads were even lower, 13.7 g and 11.9 g respectively. When a mixture of methanol and butanol was used, the results were similar to those obtained in water. It is proposed that the butanol molecule is too large to penetrate the polymer readily and therefore had little effect on its drawing behavior. In all other cases where methanol was used, its effect was equal to or greater than that of water. This brings up the question as to the relative importance of polar and non-polar bonding in the polymer on its drawing behavior and the ability of various chemicals to cause a decrease in polar and non-polar bonding in the polymer. Perhaps the explanation for the combined effect of water and methanol on drawing is that they cause a reduction in the extent of both polar and non-polar bonding in the polymer.

Berg, Guess, and Austin (12) determined that nylon sorbs 0.1508 moles of formic acid and 0.0861 moles of acetic acid per kilogram from aqueous solutions (10.0 g/l). Thus, the partition coefficients of these acids are very low (less than 1.0). At this point in the work, it was

decided that a study should be made using solutions of phenol, a chemical which is readily sorbed by the fiber from an aqueous medium. Its partition coefficient for the fiber is 15 to 17 (8). Considerable information is available concerning the sorption of phenol and the change in fiber dimensions which occur when it is sorbed (8); however, no information is available concerning the drawing of the fiber in the presence of aqueous phenol solutions.

Effect of Sorbed Phenol on the Drawing Behavior of Nylon 66

The drawing behavior of nylon immersed in aqueous phenol solutions is shown in Table 7 and Figure 4. The effect of the phenol on the yield load is small with increasing concentrations of phenol up to 5.0 g/l. At this point, the yield load decreases rapidly with increasing phenol concentration (see Figure 4).

Table 8 includes the experimentally determined concentrations of phenol in the fibers as a function of the concentration of phenol in solution. This data was used to establish the sorption isotherm shown in Figure 5. The isotherm was then used to estimate the actual amounts of phenol in the single filaments which were drawn.

The relation between the yield load and the amount of phenol sorbed is shown in Figure 6. For a phenol concentration of 50 g/l, the filament was too weak to be drawn. By extrapolating the yield load in Figure 6 to the point where its value is zero, it is found that the concentration of phenol would be approximately 8.8 moles of phenol per kilogram of nylon. It is of interest to note that this corresponds to the concentration of amide groups in the polymer. In other words, it appears that

there would be one phenol molecule for each amide-group in the polymer.

It was noted that there is an inflection in the curve shown in Figure 6 indicating that the effect of phenol on the yield stress is not a linear function of the phenol concentration. Thus, as the concentration of phenol is increased, a change in the structure of the nylon is probably occurring. To determine the concentration of phenol at which this inflection occurs, the first derivative of the curve was determined and is shown plotted against the phenol concentration in the fiber (Figure 7). It was found that the inflection occurred when the phenol concentration was 1.54 moles of phenol per kilogram of fiber. This value may correspond to the maximum number of amide sites in the polymer available for interaction with phenol without affecting the individual crystallites. Further, the magnitude of this value is probably different for nylon samples crystallized under different conditions and with different thermal histories. The number, size, and perfection of the crystallites and also the number of available amide groups is a function of the crystallization conditions for the polymer and its previous thermal history.

In the preceding discussion it was assumed that when small amounts of phenol were used, it was sorbed on specific sites, namely, those amide groups available in the polymer. Thus, the equation for a Langmuir type isotherm should be applicable:

$$\frac{1}{q} = \frac{1}{KSC} + \frac{1}{S}$$

q is the amount of phenol sorbed at equilibrium (moles per kilogram), S is the number of sites in the polymer available for sorption of phenol,

C is the equilibrium concentration of phenol (moles per liter), and K is a constant. In Figure 8, a plot of $\frac{1}{q}$ versus $\frac{1}{C}$ is shown. There appear to be two discontinuties in the curve, probably due to changes in the structure of the nylon as the concentration of phenol is increased. If a line joining the two points corresponding to the lowest initial concentrations of phenol, namely 2.5 g/l and 5.0 g/l is extrapolated to the $\frac{1}{q}$ axis, the intercept corresponding to $\frac{1}{S}$ is 0.64. Thus, the value for S is 1.56 moles per kilogram. This is interpreted as the number of amide sites available for sorption of phenol with no attendant effect on the mechanical properties of the fiber. This agrees with the value of 1.54 moles per kilogram found as the point of inflection in Figure 7. Since only two points in the isotherm were used, it is concluded that future work should include a more detailed study of the sorption of phenol at low phenol concentrations. It is interesting to note that Forward (8) also found a discontinuity in the sorption isotherm corresponding to 1.5 moles of phenol per kilogram of fiber. Forward and Palmer (13) observed a discontinuity in the absorption isotherms at 1.5 moles of phenol per kilogram of fiber. The slope of their plot of the sample length to the phenol concentration also showed a sharp change at the same point. Zaukelies (6) indicates that 1.5 moles of phenol per kilogram of fiber corresponds to very nearly two phenol molecules per unit cell vacancy assuming the density to be 1.14 g/cc and the molecular weight to be 12000, since two molecules of phenol, 140 Å^3 each, could very likely fit into each unit cell vacancy, 304 Å^3. This reoccurring break seems to indicate at this point that one absorption process is complete and another is starting.

Swelling of Nylon in Aqueous Phenol Solutions

The relationship between the yield load and the per cent volume swelling of nylon by phenol is shown in Figure 9. This curve is very similar to that in Figure 6, an inflection occurring at a volume swelling of approximately 25 per cent which, from an inspection of Figure 10, corresponds to a phenol concentration of approximately 1.5 moles per kilogram.

To determine whether the swelling of the fiber is isotropic, the longitudinal swelling was plotted against the lateral swelling (Figure 11). The swelling experiments were carried out in two ways, one with the nylon filament initially in the dry conditioned state and the other with the filament wet out with water prior to immersion in the phenol solution. In the latter case, it appears that the swelling is nearly isotropic whereas, for the dry sample, the swelling is not isotropic, the preferred swelling being in the lateral (diameter) direction for the higher concentrations of phenol. The explanation for this difference in swelling behavior is most probably the very rapid initial swelling of the outside of the dry sample which exerts a force on the inner core of the filament causing it to be oriented. Thus, the polymer would no longer be isotropic.

Effect of Sorbed Dyes on Drawing Behavior

Vickerstaff has shown that when acid dyes are sorbed by nylon the drawing load required does not change appreciably with increasing amounts of dyes; however, the breaking extension decreases appreciably when the amount of sorbed dye exceeds the amine end group content of the fiber. His interpretation of this finding is that the dye acts as a cross-link

between amide groups preventing the drawing. For very high concentrations of dye, he found that the fiber became too brittle to test (14).

In this work none of the dyes used including both acid and direct dyes caused a significant change in the drawing behavior, that is, the yield load, drawing load, and extension at break. The results are given in Tables 3, 4, 5, and 6. Thus, the results obtained here are inconsistent with those reported by Vickerstaff and no reasonable explanation for the differences are apparent.

CHAPTER V

CONCLUSIONS

The presence of water in nylon 66 has a marked effect on its drawing behavior, the yield and drawing loads for a fiber immersed in water being approximately one-half the load required for a fiber conditioned at 70° F and 65 per cent relative humidity. The addition of chemicals such as methanol, acetic acid, formic acid, and urea to water resulted in only small changes in the yield and drawing loads. These results were due to the fact that relatively low concentrations of these chemicals were used. Formic acid, for example, at sufficiently high concentrations, is a solvent for the fiber.

The effect of aqueous phenol solutions on the drawing behavior was more pronounced. As the amount of phenol sorbed by the fiber increased beyond approximately 1.5 moles of phenol per kilogram the yield load decreased in a manner proportional to the amount of sorbed phenol. An extrapolation of this curve (Figure 6) to a yield load of zero gave a value for the amount of sorbed phenol of 8.8 moles of phenol per kilogram of fiber. This value corresponds exactly to the number of amide groups in the polymer. It is concluded that one phenol molecule is associated with one amide group in the polymer.

The crystal defect model for nylon 66 as described by Zaukelies (6) is useful in explaining the results of the work described in this thesis. His model is one in which nylon is considered highly crystalline but with a high (but not unreasonably high) concentration of lattice vacancies and

dislocations. The difference between the observed density of nylon, approximately 1.14 g/cc, and its crystallographic density, 1.23 g/cc is explained by assuming that only 7.3 per cent of the lattice sites are vacant due to chain ends, chain folds, and dislocations. A confirmation of the estimate of lattice vacancies and dislocations comes from measurements of the equilibrium sorption of phenol by nylon (11). There was found a discontinuity in the sorption isotherm corresponding to a phenol concentration of 0.17 moles of phenol per mole of the amide group. This discontinuity was interpreted as the point of the completion of one sorption process and the beginning of a new sorption process (6).

From Figure 7, it was noted that the point at which the maximum change in the yield load with respect to phenol concentration occurs at a point corresponding to approximately 0.17 moles of phenol per mole of amide groups. Thus, this interpretation of the mechanical properties of nylon containing phenol adds support to the crystal defect model.

As discussed in Chapter IV and shown in Figure 8, the number of sorption sites on nylon which can be occupied without affecting its drawing behavior was found to be 0.17 moles of phenol per mole of amide groups. Thus, nylon can sorb approximately 1.6 moles of phenol per kilogram of fiber before there is any appreciable effect on the yield load. When this concentration of phenol is exceeded, a different sorption process is operative, namely, the attack of the more highly ordered (crystalline) regions of the fiber resulting in a rapid decrease in the yield load.

The total per cent swelling of nylon in aqueous phenol solutions is almost the same regardless of whether the measurements are made with a initially dry sample or a sample initially wet with water. Starting with

a dry sample gives a preferred swelling in the lateral direction and probably a preferred molecular orientation. Starting with a wet sample gives swelling that is almost isotropic and probably with no preferred molecular orientation.

The presence of dyes in the nylon does not produce any significant changes in the yield load or the drawing load. In dyeings made at low pH values in this work all the amine groups should have had dye molecules attached to them. It was concluded that the amine groups do not play a significant role in the drawing of the nylon.

CHAPTER VI

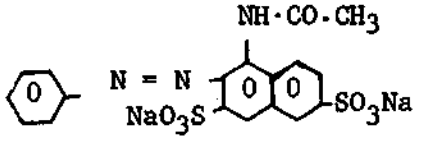
RECOMMENDATIONS

In further studies of this subject, the concentrations of acids and urea in water should be increased. The concentrations should be increased to a point where a yield stress of zero could be determined. The characteristic swelling of nylon in the acids and urea would also be of interest.

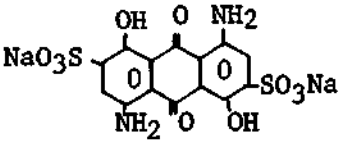
In order to give a better interpretation of the effect of phenol on the drawing behavior of nylon, it would be informative to determine by x-ray and birefringence measurements what structural changes occur as a consequence of the treatments.

Table 1. Dye Structures

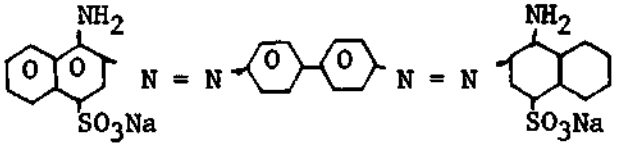
C. I. Acid Red 1 (C. I. 18050)



C. I. Acid Blue 45 (C. I. 63010)



C. I. Direct Red 28 (C. I. 22120)



C. I. Direct Blue 1 (C. I. 24410)

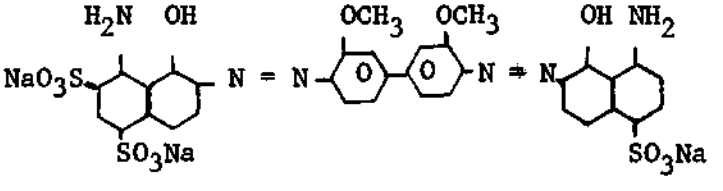


Table 2. Solutions

Solution Tested In	pH	No. of Tests	Yield Load (g)	Stand. Dev. (g)	Drawing Load (g)	Stand. Dev. (g)	Yield Load / Drawing Load
Air		10	30.3	.35	28.3	.35	1.07
H_2O	5.6	5	17.2	.27	15.1	.22	1.14
0.001N HCL	3.2	4	17.1	.25	15.0	0	1.14
0.01N HCL	2.2	4	17.0	0	15.1	.25	1.13
0.1N HCL	1.3	1	17.0	-	15.0	-	1.13
1g/l Acetic	3.5	5	16.9	.21	14.4	.06	1.17
4g/l Acetic	3.2	6	16.6	.25	14.2	.10	1.17
8g/l Acetic	2.9	2	17.0	.07	14.8	0	1.15
10g/l Acetic	2.8	4	17.0	.17	14.8	.25	1.15
12g/l Acetic	2.8	2	17.25	.07	15.0	0	1.15
20g/l Acetic	2.6	1	17	-	15.0	-	1.13
50g/l Acetic	2.4	2	16.4	.21	14.4	0	1.14
100g/l Acetic	2.2	1	16	-	14.0	-	1.14
.5g/l Formic	3.0	3	17.0	0	15.0	0	1.13
4g/l Formic	2.5	3	16.8	.29	15.0	0	1.12

Table 2. Solutions (Continued)

Solution Tested In	pH	No. of Tests	Yield Load (g)	Stand. Dev. (g)	Drawing Load (g)	Stand. Dev. (g)	Yield Load / Drawing Load
20g/l Formic	2.1	1	17.1	-	14.6	-	1.17
200g/l Urea	-	2	17.0	0	14.5	0	1.17
Methanol	7	5	15.3	.45	13.3	.22	1.15
50% Butanol 50% Methanol	7.1	4	17.5	.11	14.5	.05	1.20
50% H_2O 50% Methanol	4.5	3	13.7	.06	11.9	0	1.15
10g/l Acetic in 50% H_2O 50% Methanol	3.3	4	14	.22	11.9	.15	1.18
20g/l Acetic in 50% H_2O 50% Methanol	3.2	3	13.7	.15	11.8	.12	1.16
10g/l Acetic in Methanol	4	5	15.3	.20	13.2	.15	1.16
20g/l Acetic in Methanol	3.9	3	15.2	.10	13.1	.06	1.17
20g/l Formic in Methanol	3.4	3	14.8	.25	12.6	.10	1.18

Table 3. Results of Dyeing With C. I. Acid Red 1

Amount of Acid in Dye Bath	Weight of Nylon In Grams	pH	Yield Load (g)	Stand. Dev. (g)	Drawing Load (g)	Stand. Dev. (g)	Yield Load / Drawing Load
25 ml of H_2O	0.2535	9	28.5	0	27	0	1.06
25 ml of .5g/l Acetic	0.2539	4.2	28.5	.11	27	0	1.06
25 ml 1g/l Acetic	0.2556	3.8	28.9	.08	27.3	.14	1.06
25 ml 2g/l Acetic	0.2560	3.6	28.9	.24	27.3	.24	1.06
25 ml .5g/l Formic	0.2562	3.3	28.9	.19	27.5	.31	1.05
25 ml 1g/l Formic	0.2569	3.1	29	.26	27.8	.24	1.04
25 ml 2g/l Formic	0.2574	2.9	27.1	.09	26.2	0	1.03
25 ml 0.02N HCL	0.2574	2.2	28.7	.29	27.6	.15	1.04
25 ml 0.2N HCL	0.2605	1.1	29.5	0	28	0	1.05

Table 4. Results of Dyeing With C. I. Acid Blue 45

Amount of Acid in Dye Bath	Weight of Nylon In Grams	pH	Yield Stress (g)	Drawing Stress (g)	Yield / Drawing	% Dye Taken Up
25 ml .5g/l Formic	.2494	3.3	28.7	27	1.06	.85%
25 ml 1g/l Formic	.2506	2.9	28.6	27	1.06	1.05%
25 ml 2g/l Formic	.2544	2.7	28.6	27	1.06	1.06%
25 ml 0.01N HCL	.2521	2.4	28.9	27.1	1.07	1.11%
25 ml 0.1N HCL	.2543	1.6	28.9	27	1.07	1.24%
25 ml 0.1N H_2SO_4	.2556	1.5	28.8	27	1.07	1.36%

Table 5. Results of Dyeing With C. I. Direct Red 28

Treatment	Yield Load (g)	Stand. Dev. (g)	Drawing Load (g)	Stand. Dev. (g)	Yield Load / Drawing Load
2% o.w.f. boiled under reflux with nylon 24 hrs.	29.7	.42	28.2	.29	1.05
10% o.w.f. boiled under reflux with nylon 24 hrs.	30.1	.12	28.3	.29	1.06
Nylon from 10% o.w.f. above was boiled 1 hr. in 0.02N HCL	30.2	.10	28.4	.17	1.07

Table 6. Results of Dyeing With C. I. Direct Blue 1

Treatment	Yield Stress (g)	Stand. Dev. (g)	Drawing Stress (g)	Stand. Dev. (g)	Yield Drawing
2% o.w.f. boiled under reflux with nylon for 24 hrs. with 15% Acetic Acid	30	0	28.3	.35	1.06
10% o.w.f. boiled under reflux with nylon for 24 hrs. with 15% Acetic Acid	30.7	.21	28.5	.35	1.08
Nylon from 10% o.w.f. above was boiled 1 hr. in 0.02N HCL	30.6	.49	28.7	.49	1.07

Table 7. Effects of Phenol on the Drawing of Nylon 66

Concentration of Phenol g/l	pH	No. of Tests	Yield Load (g)	Stand. Dev. (g)	Drawing Load (g)	Stand. Dev. (g)	Yield Load / Drawing Load
0	5.6	5	17.2	.27	15.1	.22	1.14
2.5	4.6	6	17.2	.17	15.3	.18	1.13
5	4.5	6	16.8	.11	15.5	.14	1.08
7.5	4.4	6	15.8	.04	15.1	.07	1.05
10	4.3	5	14.6	.22	14.1	.23	1.03
20	4.2	5	9.2	.12	9.2	.12	1.00
30	4.2	6	5.4	.22	didn't draw		
40	4.1	5	3.14	.13	didn't draw		
50	4.0	too weak					

Table 8. Amount of Phenol Absorbed by Nylon 66

Concentration of Phenol g/l	Weight of Fiber (g)	Partition Coefficient	Concentration in Bath g/l	Absorbed by Nylon g/kg
2.5	1.0279	18.5	1.79	33.11
5	1.0226	14.8	3.86	57.13
7.5	1.0140	14.2	5.79	82.22
10	1.0125	15.0	7.64	114.60
20	.9960	11.7	15.87	185.68
30	1.0118	13.9	23.62	328.32
40	1.0115	14.9	31.41	468.01
50	1.0045	16.0	38.47	615.52

Table 9. Dimensional Changes in Nylon as a Result of the Sorption of Phenol Starting With Dry and Wet Nylon 66

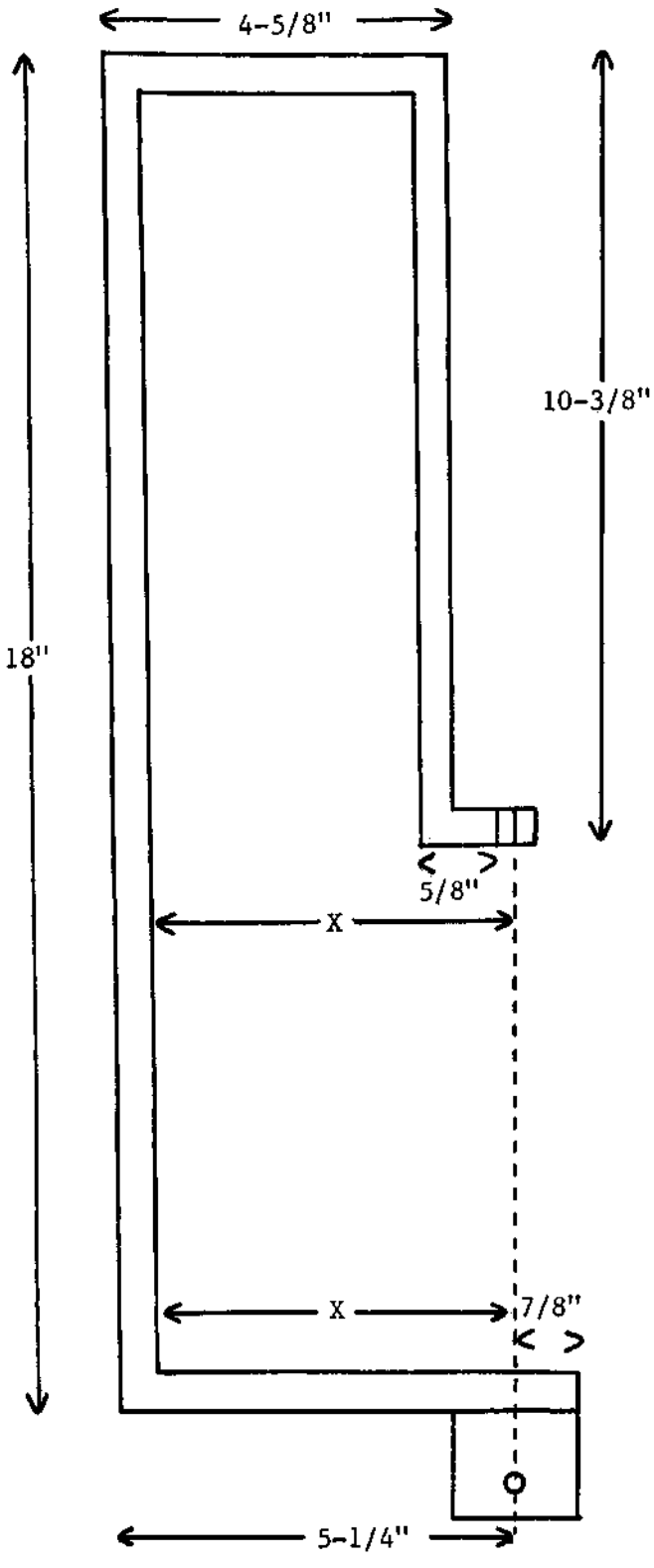
Phenol g/l	Starting with dry sample		Starting with sample throughly wet with H_2O	
	Length Increase	Diameter Increase**	Length Increase	Diameter Increase**
0	2.5%*	3.1%	---	---
2.5	3.9%	4.9%	---	---
5	4.2%*	6%	---	---
7.5	5.4%	7.3%	---	---
10	6.1%*	8.5%	5.1%	7.93%
20	9.1%*	9.7%	8.9%	11.75%
30	14%*	15.8%	15.4%	16.95%
40	15.3%*	29.5%	22.3%	21.76%
50	15.5%*	34.7%	---	---

*Average value of 2 trials, difference in two values being no more than 0.5%.

**All diameter measurements are the average of 10 values with no variations of more than 0.2%.

Table 10. Elongation of Nylon 66 as a Result of Increasing Phenol Concentration

Concentration of Phenol g/l	Time for Equilibrium	% Extension			
		Sample 1	Sample 2	Sample 3	Sample 4
0	30 minutes	2.6	2.7	2.8	2.7
2.5	50 minutes	3.1	3.4	3.1	3.1
5	40 minutes	3.3	3.4	3.5	3.4
7.5	50 minutes	4.1	4.1	4.2	4.1
10	80 minutes	5.1	5.1	5.2	5.1
20	80 minutes	---	8.9	9.1	8.9
30	70 minutes	---	---	15.7	15.4
40	60 minutes	---	---	---	22.3



Notes:

Frame from 5/8" square #316 Stainless Steel Bar stock.

Distances marked X must be exactly equal.

Figure 1. Diagram of Lower Clamp for Instron

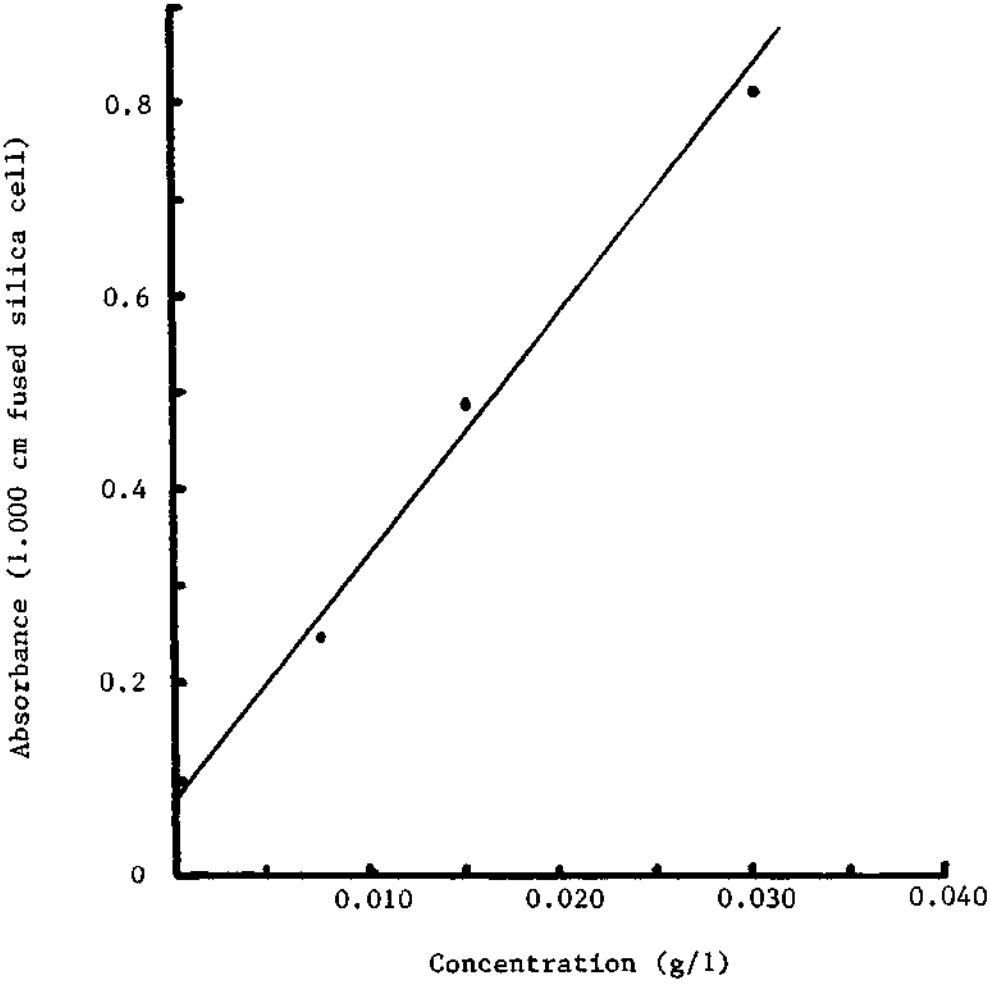


Figure 2. Calibration Curve for Acid Blue 45

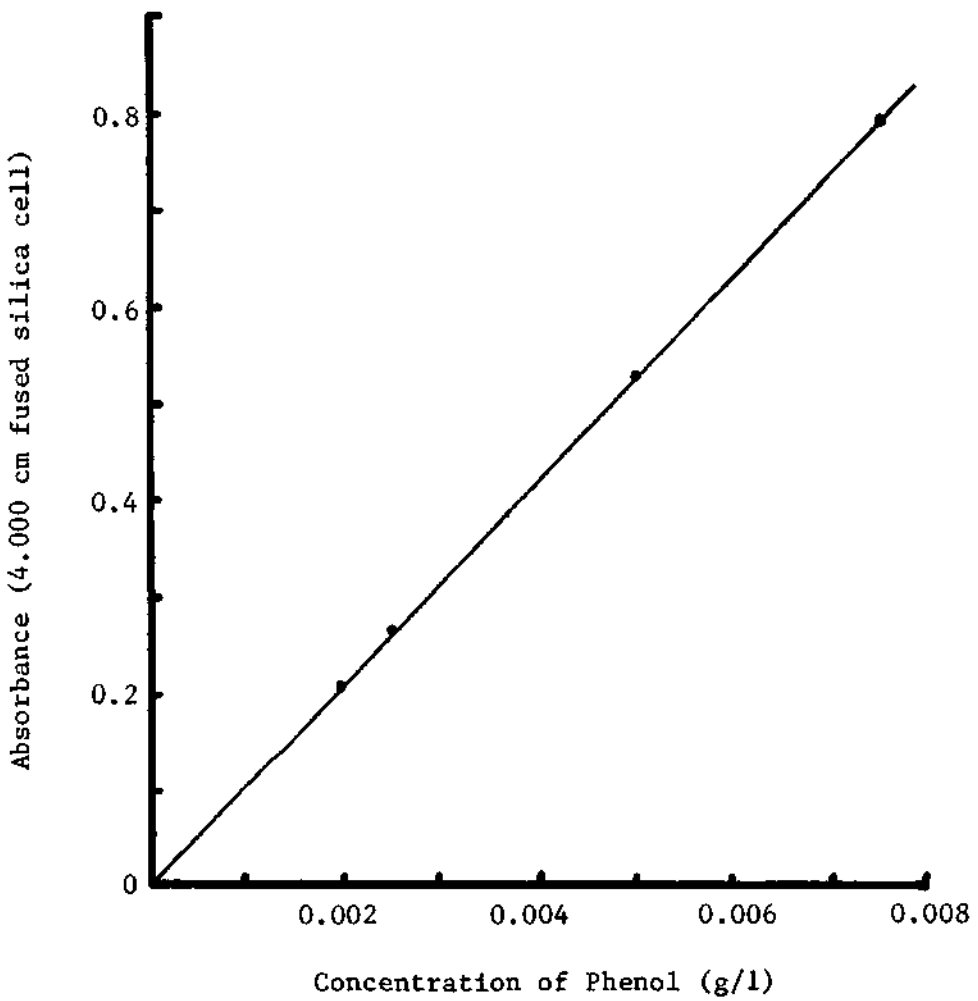


Figure 3. Calibration Curve for Phenol

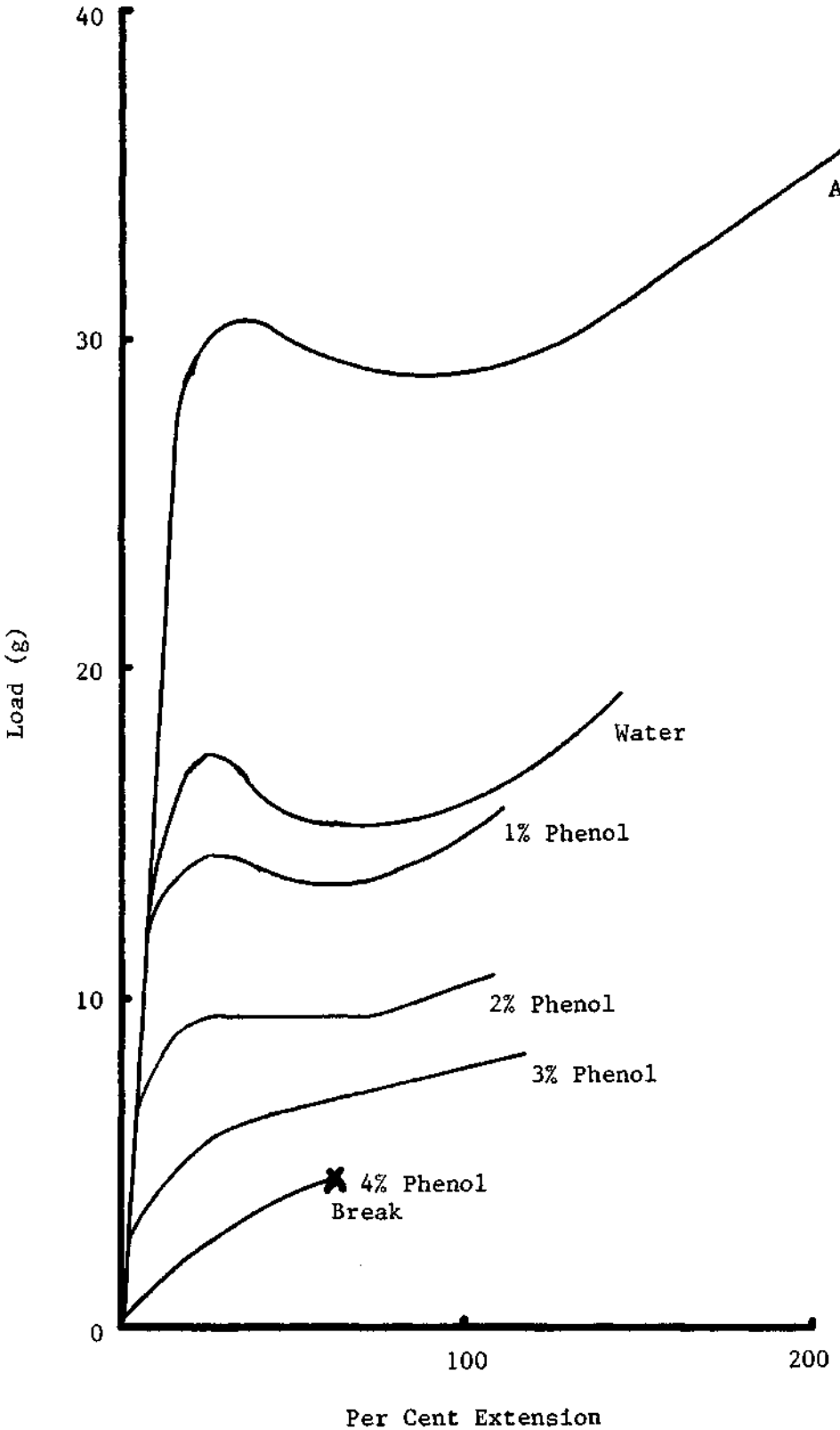


Figure 4. Typical Stress-Strain Curves

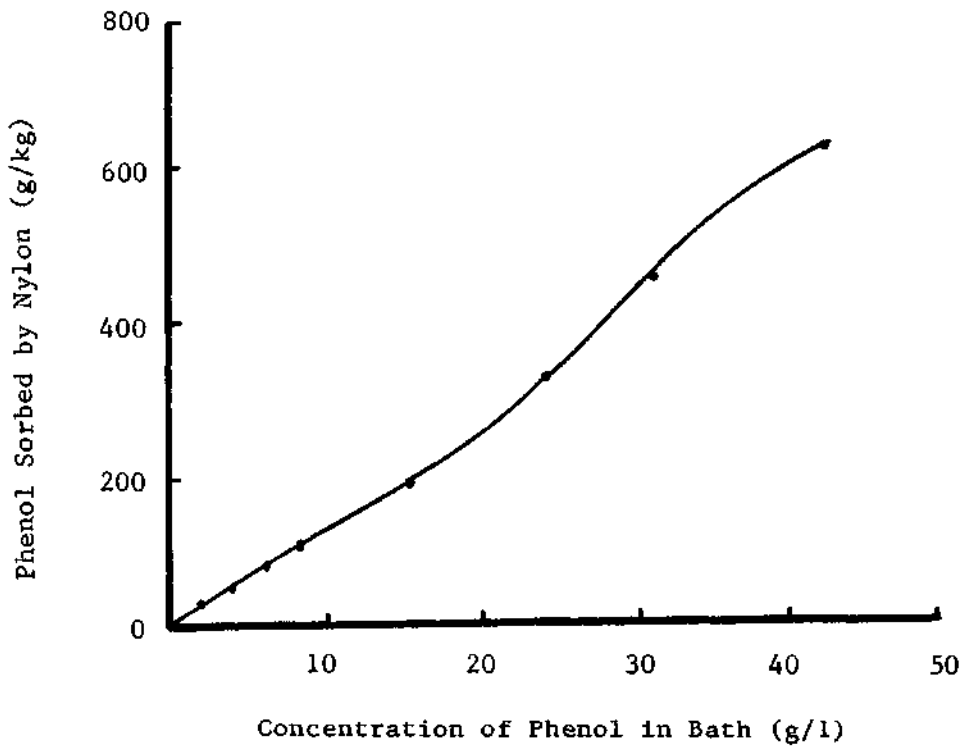


Figure 5. Phenol Absorbed Versus Concentration of Phenol

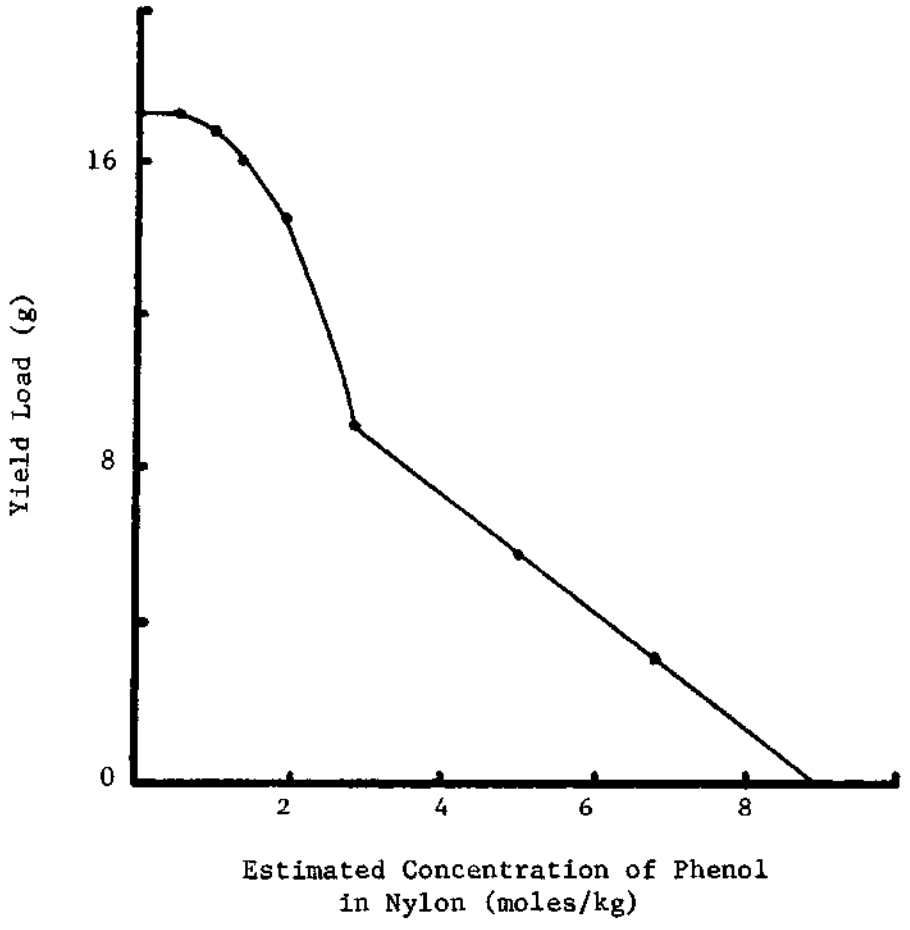


Figure 6. Yield Load Versus Phenol Concentration in Nylon

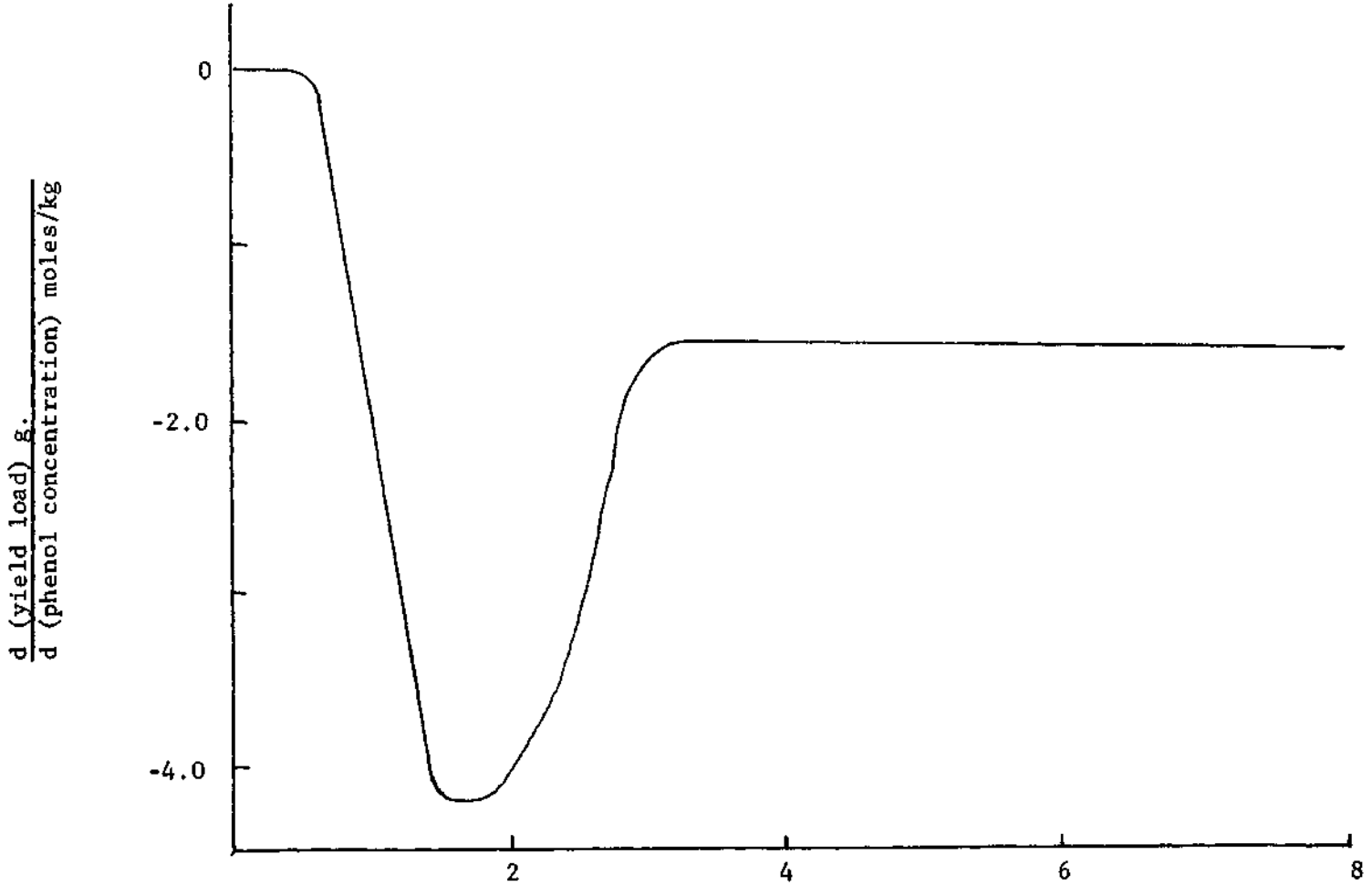


Figure 7. Inflection of Yield Stress Versus Phenol Concentration

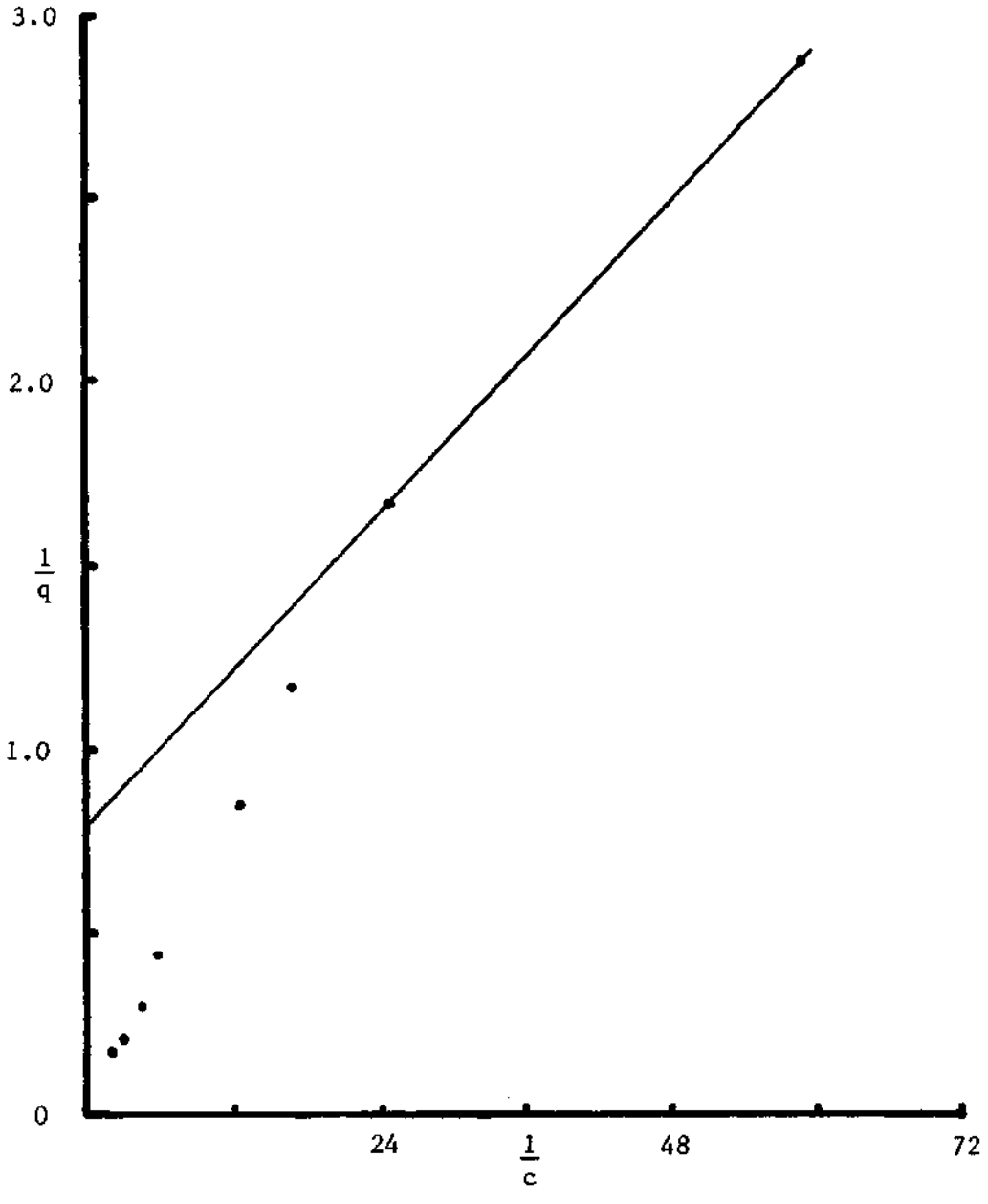


Figure 8. Langmuir Sorption Isotherm for Phenol and Nylon 66

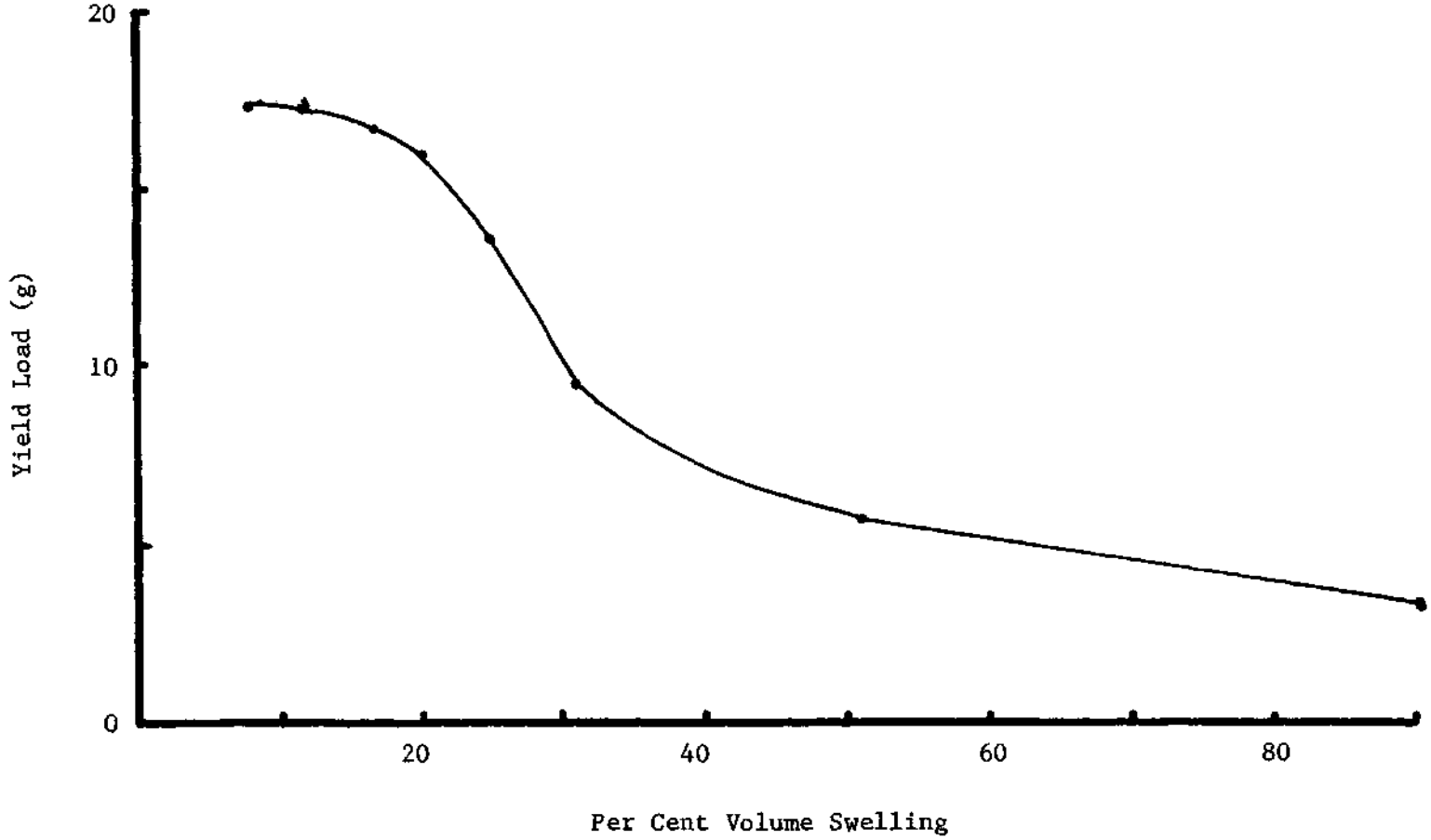


Figure 9. Yield Load Versus Per Cent Volume Swelling

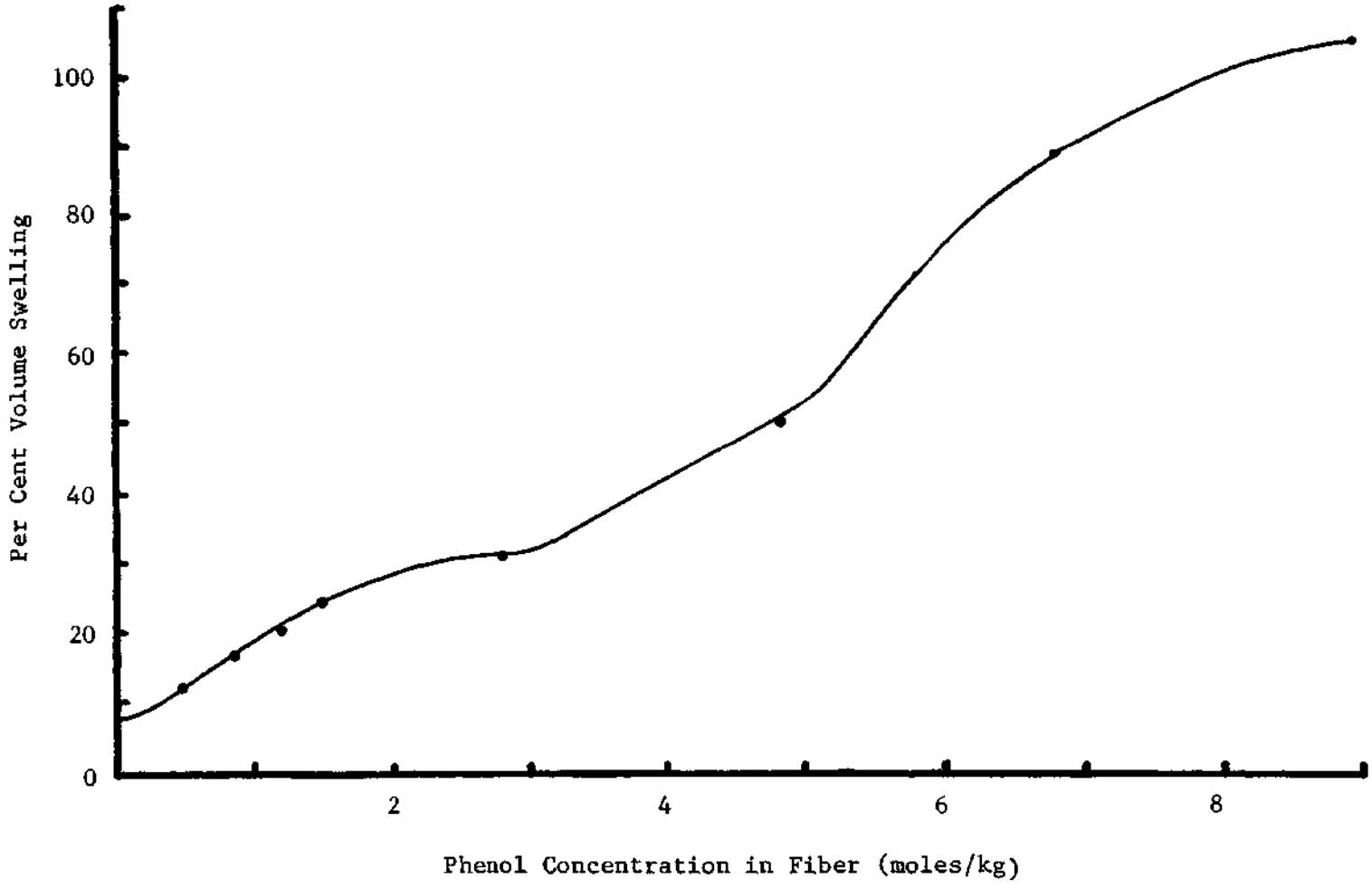


Figure 10. Per Cent Volume Swelling Versus Phenol Concentration in Nylon

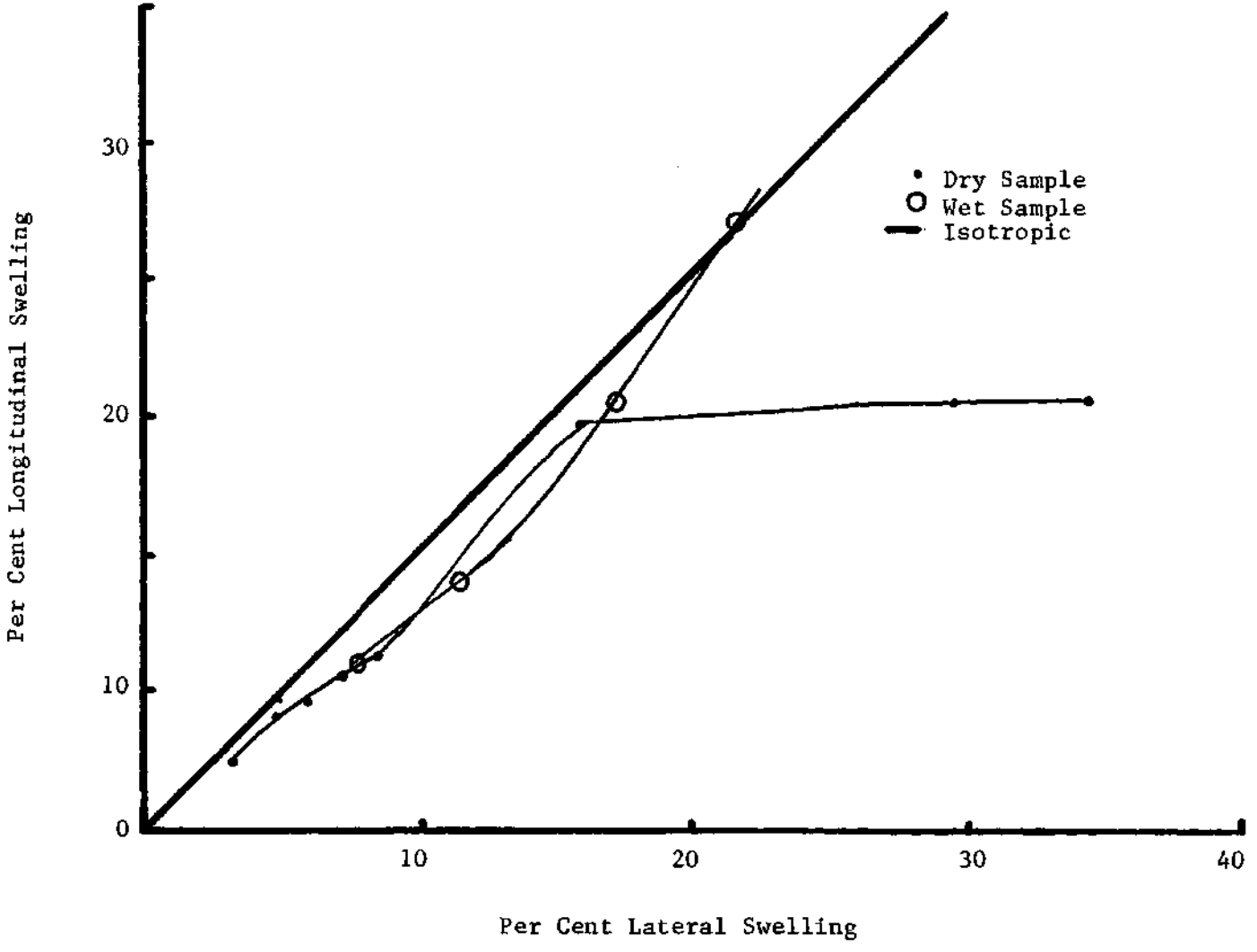


Figure 11. Swelling of Nylon Starting With Wet and Dry Samples

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